

SUMMARY AND CONCLUSIONS

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The present investigation deals with the studies on the preparation, characterization and catalytic activity of polymer bound metal complex catalysts. The catalytic activity of the prepared catalysts has been investigated for two model reactions (viz hydrogenation and oxidation) giving emphasis on the stability of metal chelates on the polymer bound and unbound metal chelates.

The thesis has been divided into five chapters,

Chapter - I contains a brief literature survey on homogeneous, heterogeneous as well as on supported metal complex catalysts, advantages and disadvantages of both homogeneous and heterogeneous catalysts, progress in the studies of immobilization and types of supports used for anchoring metal complexes.

Chapter - II includes the experimental details of the functionalization of crosslinked polymer (i.e. styrene-divinyl benzene), ligand introduction and the anchoring of the metal in the suitable form on the surface. The various physical properties such as bulk density, moisture content, swelling behaviour and surface area for the anchored catalysts have been studied. The modern techniques viz. UV-Vis, IR, FTIR, SEM and ESR have also been included for the characterization of the catalysts. The experimental procedures as well as the reactor employed for the kinetics of the hydrogenation and oxidation reactions have been discussed in detail.

Chapter - III describes physico-chemical characterization of the polymer support and supported metal complex catalysts. Surface area and the pore volume of the supports and the catalysts have been measured using BET method at liquid N₂ temperature. The morphology of the catalysts has been seen by scanning electron microscope. The mode of anchoring of metal chelates onto polymer support has been arrived at by elemental analyses, UV-Vis reflectance spectroscopy, IR, FTIR and ESR. Selection of the solvent for catalytic study has been made on the basis of swelling studies. The thermal stability of the catalysts and the supports has been investigated using DTA and TG analyses. On the basis of available evidences, probable structures for the polymer anchored catalysts have been proposed.

The study of kinetics of the hydrogenation of nitrobenzene catalysed by these metal complex catalysts is included in Chapter-IV. The influence on the rate of the reaction of various factors such as substrate and catalyst concentration, temperature and the effect of different solvents has been investigated. Experiments were also carried out with metal complex catalysts in homogeneous system and the results have been compared with respective heterogenised-homogeneous systems. On the basis of the kinetic data, the values for energy of activation and entropy of activation have been calculated. A probable reaction mechanism has been proposed on the basis of the literature survey as well as experimental evidences. Recycling efficiency of the catalysts is also included.

Chapter - V includes the kinetics of oxidation of toluene to benzaldehyde to investigate the catalytic activity of some of

the synthesised catalysts. The effect on the rate of various factors e.g. the substrate and the catalyst concentration, temperature of the system as well as the variation of the solvents has been studied. A probable reaction mechanism has been proposed. Recycling efficiency of the catalysts has also been studied to investigate the stability of the catalysts. On the basis of the above results the following conclusions have been made.

Styrene-divinyl benzene copolymer offers the advantage of high purity catalysts support which can be easily functionalized. This polymer was found to be thermally stable upto $\sim 140^{\circ}\text{C}$. Controlled synthesis permits systematic variation of physical form, crosslinking and the nature of the functional groups. Incorporation of the catalytically active component is possible by the treatment of solution of metal salt with functionalized polymer under suitable conditions. Chelation of the metal complexes on the polymer matrix is ensured by functionalising the macroporous beads using suitable functional group, by choosing a good swelling agent, incorporating efficient chelating ligands and allowing sufficient time for the complexation

Characterization of the supports as well as the polymer bound catalysts is possible by utilizing the conventional techniques such as elemental analysis, moisture content, bulk density measurement and swelling studies. The mode of anchoring of metal complexes onto the polymer matrix can be ascertained by the detailed spectroscopic studies of polymer supports, functionalized polymer supports, polymer bound metal complexes and unbound metal complexes. The change in

morphology of the support after complexation is revealed by SEM and surface area measurement.

Polymer bound metal complexes exhibit good catalytic activity for the hydrogenation of nitrobenzene to aniline. An enhanced rate of hydrogenation was observed in the case of polymer bound complexes as compared to unbound complexes probably due to the formation of an intermediate surface active hydrido complex. The order of reaction was found to be fractional with respect to the substrate as well as the catalyst concentration which might be due to the non-accessibility form of the catalytic sites and the steric hindrance due to the chelating ligand molecules. The values for the energy of activation and entropy of activation have been calculated using kinetic data. The negative value of entropy of activation is indicative of the fact that there is considerable loss of freedom due to fixation of the catalyst molecules on the surface of the polymer.

The catalytic activity of polymer bound metal complexes of L-2 amino butanol was found to be better than that of the glycine counterparts. Study was made using polar as well as non-polar solvents and an enhanced rate was observed as the nature of the solvent varies from non-polar to polar character. This may be due to higher swelling as well as moderate coordinating ability of the solvent with the metal species. The stability of the catalysts was seen by studying the recycling efficiency of the catalysts. The most of the catalysts were found to be stable upto four cycles.

Some of the synthesised catalysts were also used to investigate the catalytic behaviour for the oxidation of toluene

to benzaldehyde by varying the parameters such as the temperature of the system and the concentration of the catalyst and the substrate. A higher activity was observed with heterogenised homogeneous catalyst, which might be due to formation of oxo and peroxo complexes on the surface of the support. The probable reaction mechanism was proposed on the basis of experimental evidences and literature survey for hydrogenation of nitrobenzene and oxidation of toluene.

The study thus shows that better catalytic activity could be achieved by proper selection of the polymer support, chelating ligand, swelling agent and the active component to synthesise heterogenised homogeneous catalysts for a given reaction with several advantages over their homogeneous counterparts. This was the primary objective of the thesis.